

UDC 666.293.522.53:666.232.6

SYNTHESIS OF SPINEL-BASED CERAMIC PIGMENTS FROM HYDROXYCARBONATES

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Translated from *Steklo i Keramika*, No. 9, pp. 21–24, September, 2004.

A technology for the production of pigment based on spinel $\text{Co}_{1-x}\text{Mg}_x\text{Al}_2\text{O}_4$ is developed, where $0.67 \leq x \leq 0.80$. The pigment has a bright blue color and is identical to the reference standard, although its cobalt content is 2–3 times lower.

Many ceramic pigments constitute spinel-type compounds with the general formula $\text{M}^{2+}\text{M}_2^{3+}\text{O}_4$, where the bivalent metal is cobalt or partly replacing it zinc or magnesium and the trivalent material is aluminum or chromium, which replaces it. These are pigments of blue-light blue or blue-green colors that can be used in paint and lacquer composites. Spinel is mixed M^{2+} and M^{3+} oxides and coordination polymers, whose crystals consist of tetrahedral M^{2+}O_4 and octahedral M^{3+}O_6 structural units. Their crystal structure corresponds to a cubic face-centered lattice: the ions O^{2-} located at the lattice points form a compact cubic packing.

Such spinels are usually synthesized by high-temperature treatment (1300–1400°C) of oxides after their preliminary mechanical treatment in mills, which is disadvantageous due to the high energy consumption in this technology [1]. Therefore, in order to decrease the temperature of synthesis of spinels, highly dispersed initial oxides or their homogenized mixtures are used, which is attained by spraying aqueous solutions of salts and their subsequent drying and thermal treatment, or by the method of coprecipitation of bi- and trivalent metal ions in the form of hydroxides, carbonates, or base carbonates (U.S. patent No. 4979991 and Poland patent No. 143393).

The highest degree of homogenization is achieved by heat treatment of complex salt solutions. It can be assumed that the production of spinels from ammonia hydrocomplexes will make it possible to substantially decrease the temperature of their formation and increase the product yield.

The purpose of our study was to investigate the effect of the conditions of precipitation and thermal treatment of ammonia hydroxycarbonates on the formation of spinels of the type $\text{Co}_{1-x}\text{M}_x\text{Al}_{2-y}\text{Cr}_y\text{O}_4$ and their color range.

The initial reactants were of grades “chemically pure” and “analytically pure”: The precipitation of ammonia hydroxycarbonates was performed by drop introduction of 0.2-M solutions of metal sulfate salts into a 2-M solution of NH_4HCO_3 heated to 60–75°C, in accordance with the procedure described in [2]. The content of Co^{2+} , Al^{3+} , Mg^{2+} , and Zn^{2+} in hydroxycarbonates was determined by the trilonometric method; Cr^{3+} by the titrimetric method using Mohr’s salt with preliminary conversion into Cr^{6+} ; the content of NH_4^+ by the photometry method; the content of SO_4^{2-} groups by the gravimetric method [3]; the content of CO_3 by the volumetric method recovering carbon dioxide in an alkali solution after heating at a temperature of 220–250°C of samples dried at room temperature [4]; and the content of the sum of OH and CO_3 groups by the oxalate method.

The samples were analyzed using the following methods: IR spectroscopy using a JR-475 spectrophotometer produced by Shimadzu (samples were compressed in tablets with KBr); differential thermal analysis using a MOM derivatograph with a heating rate of 10–11 K/min in the temperature interval of 20–1000°C for a sample of 500 mg; x-ray phase analysis using a DRON-3M diffractometer with CuK_α radiation (nickel filter); interplanar distance d/n were calculated based on the gravity center of the diffraction maximums; the elementary cell parameters of spinels were determined based on the lines hkl 220, 222 according to the formula for the face-centered cubic lattice:

$$a = \frac{\lambda}{2} \sin \theta \sqrt{h^2 + k^2 + l^2},$$

With the measurement error not exceeding ± 0.005 and ± 0.004 Å, respectively. The color characteristics were determined according to the data in [5].

The main regularities of the synthesis of spinels from ammonia hydroxycarbonates of metals are described in [6].

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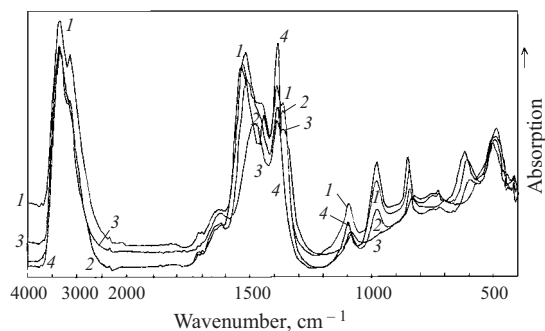
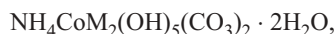


Fig. 1. IR spectra of samples of ammonia hydroxycarbonates of Co(II), Al(III), and Cr(III) with molar ratios Co : Cr : Al equal to 1 : 1 : 1 (1), 1 : 1.5 : 0.5 (2), 1 : 2 : 0 (3), and 1 : 0 : 2 (4).

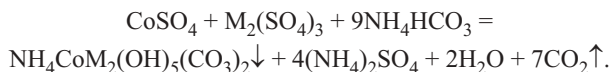
It follows from the results of IR spectroscopy and chemical analysis that precipitated ammonia hydroxycarbonates of Co^{2+} , Al^{3+} , and Cr^{3+} contain five hydroxyl groups and two carboxyl groups and have the common formula:



where M is Cr^{3+} and Al^{3+} .

The conditions of synthesis, the filtering rate, and the composition of hydroxycarbonates are listed in Table 1.

The summary reaction of precipitation of hydroxycarbonates can be represented as follows:



It is known that the process of the formation of polymeric structures with OH-bridge bonds takes place in the

course of precipitation of Cr(III) and Al(III) in the form of hydroxy salt or hydroxides [7]. This is corroborated by the IR spectroscopic studies (Fig. 1). The absorption bands (AB) at $980 - 1100 \text{ cm}^{-1}$ related to hydroxyl groups prove the existence of bridge OH^- bonds in the structure. Furthermore, there are AB typical of the group CO_3^{2-} of the monodentate coordination (845 and 1100 cm^{-1} – valence vibration of C – O bond, $1360 - 1390 \text{ cm}^{-1}$ – symmetrical valence vibration of CO_2 , $1445 - 1530 \text{ cm}^{-1}$ – asymmetric valence vibration of CO_2) and bidentate coordination, which is evidenced by the duplication of bands in the range of $1445 - 1530$ and $1360 - 1390 \text{ cm}^{-1}$. Consequently, one of CO_3^{2-} groups in the polymer chain replaces the bridge OH group.

The presence of H_2O is corroborated (AB with deformation vibration 1630 cm^{-1} and valence vibration 3450 cm^{-1}) and OH-groups (AB of valence vibration 3150 cm^{-1}).

The highest intensity of the bands of the deformation vibrations of C – O bond (845 and 980 cm^{-1}) is registered in hydroxycarbonate samples containing Al^{3+} , which points to a stronger bond acting as the bridge bond. As the concentration of Cr^{3+} replacing Al^{3+} grows, the band intensity decreases.

Comparing the investigated series of the compounds, the most evident duplication of the AB in the range of symmetric valence vibration $1360 - 1390 \text{ cm}^{-1}$ and asymmetric valence vibration $1445 - 1530 \text{ cm}^{-1}$ of CO_3 is registered in $\text{NH}_4\text{CoCr}_2(\text{OH})_5(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$, which points to stronger C – O bonds in the structural fragment $\text{Cr} - \text{O} - \text{C} - \text{O} - \text{Co}$ implemented via the CO_3^{2-} group.

The studies of the precipitation conditions of hydroxycarbonates established that a temperature interval of $60 - 75^\circ\text{C}$ ought to be maintained for the formation of

TABLE 1

Sample	Molar ratio of components	Precipitation temperatures, °C	Precipitation pH	Filtration rate, ml/(min · cm ²)	Mass content, %					Empirical formula
					Co	Al	Cr	CO ₂	H ₂ O	
	Co : Cr : Al:									
1a	1 : 1 : 1	60 – 75	8.30	2.10	15.6	7.1	13.7	14.6	14.4	NH ₄ CoAlCr(OH) ₅ (CO ₃) ₂ · 2H ₂ O
1b	1 : 1 : 1	40 – 55	8.50	0.53	15.5	7.0	13.5	11.6	15.5	NH ₄ CoAlCr(OH) ₇ CO ₃ · 2H ₂ O
1c	1 : 1 : 1	60 – 70	8.60	0.08	15.5	7.0	13.4	11.1	15.8	The same
2	1 : 1.5 : 0.5	60 – 75	8.40	0.82	15.1	3.4	19.9	14.2	14.0	NH ₄ CoAl _{0.5} Cr _{1.5} (OH) ₅ (CO ₃) ₂ · 2H ₂ O
3	1 : 2 : 0	60	8.75	0.77	14.6	–	25.7	13.7	18.4	NH ₄ CoCr ₂ (OH) ₅ (CO ₃) ₂ · 2H ₂ O
4	1 : 0 : 2	60	8.30	1.22	16.6	15.2	–	15.6	9.0	NH ₄ CoAl ₂ (OH) ₅ (CO ₃) ₂ · 2H ₂ O
5	1 : 0 : 2.5	60	8.10	5.68	14.8	17.0	–	18.0	8.5	NH ₄ CoAl ₂ (OH) ₅ (CO ₃) ₂ · 2H ₂ O + 0.25Al ₂ (OH) ₂ (CO ₃) ₂
6	1 : 0.5 : 1.5	60	8.50	3.37	16.5	11.3	7.3	15.0	13.0	NH ₄ CoAl _{1.5} Cr _{0.5} (OH) ₅ (CO ₃) ₂ · 2H ₂ O
7	Co : Al : Zn = 1 : 3.5 : 0.25	60	7.90	10.30	10.5	18.0	2.9 Zn	19.0	9.5	NH ₄ Co _{0.8} Zn _{0.2} Al ₂ (OH) ₅ (CO ₃) ₂ · 2H ₂ O + 0.25Al ₂ (OH) ₂ (CO ₃) ₂
8	Co : Al : Mg = 0.25 : 2.5 : 1	60	8.00	6.09	3.7	17.0	6.0 Mg	18.0	10.0	NH ₄ Co _{0.2} Mg _{0.8} Al ₂ (OH) ₅ (CO ₃) ₂ · 2H ₂ O
	Co : Al : Mg:									
9	0.1 : 2.1 : 1	70	7.90	3.89	1.9	17.2	6.9 Mg	18.0	12.0	NH ₄ Co _{0.09} Mg _{0.91} Al(OH) ₅ (CO ₃) ₂ · 2H ₂ O
10	1 : 4 : 1	70	7.70	3.27	9.0	16.5	3.7 Mg	16.5	13.0	NH ₄ Co _{0.5} Mg _{0.5} Al(OH) ₅ (CO ₃) ₂ · 2H ₂ O
11	0.5 : 3 : 1	60	7.90	5.62	6.1	16.8	5.0 Mg	18.0	12.0	NH ₄ Co _{0.33} Mg _{0.67} Al(OH) ₅ (CO ₃) ₂ · 2H ₂ O

well-formed and fast-filtering hydrocarbonate precipitate. Precipitation of hydroxycarbonates at a temperature below 60°C results in the formation of highly aqueous precipitates with low filterability, and above 75°C — in the decomposition of hydroxycarbonates and, accordingly, in the formation of metal hydroxides instead of hydrocarbonates, which is corroborated by the chemical analysis data. Furthermore, decreasing the temperature below 60°C subsequently results in the formation of spinels with dull nonsaturated colors.

Another essential factor in the precipitation of hydroxycarbonates is the pH of the solutions. With pH of the solution below 7.5 metal ions precipitate in the form of hydroxides. As the pH increases over 8.5, partial dissolution of hydroxycarbonate precipitate is observed with the formation of the soluble complex salt $\text{Co}(\text{NH}_3)_6\text{SO}_4$ and hydroxides AlOOH , $\text{Cr}(\text{OH})_3$.

Although ammonia hydroxycarbonates are x-ray amorphous, it is logical to assume that the structure of their bonds has the protospinel type and facilitates the conversion into spinel in heat treatment, which lowers the temperature of synthesis.

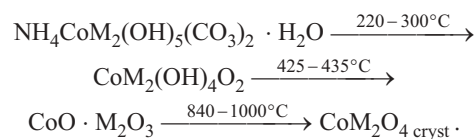
The thermal curves of ammonia hydroxycarbonates of metals exhibit a wide endothermic effect with a minimum of 220–250°C related to the weight loss from 41.2 to 47.8% due to the removal of CO_2 , NH_3 , and water. The valence absorption of OH groups persists (AB 3450 cm^{-1}). The isothermal exposure at a temperature up to 700°C determines the complete removal of OH-groups, where the weight loss ranges from 55.4 to 61.0%. The beginning of the formation of the spinel phase is registered at a temperature of 800°C, which is confirmed by the x-ray phase analysis data.

For hydroxycarbonates containing Cr^{3+} , for instance $(\text{NH}_4\text{CoAl}_{0.5}\text{Cr}_{1.5}(\text{OH})_5(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O})$, $(\text{NH}_4\text{CoAlCr}(\text{OH})_5(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O})$, $(\text{NH}_4\text{CoCr}_2(\text{OH})_5(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O})$, a slight exothermic effect is registered at a temperature of 425–435°C, presumably determined by the partial formation of chromium ox-

ide (III). A slight endothermic effect with a minimum at 800–840°C related to the crystallization of spinel is observed in all hydroxycarbonate samples. The end product of thermolysis is spinel. The IR spectra of spinel bands exhibit the AB (510, 530 cm^{-1}) responsible for the M–O bond. The highest intensity of the absorption band of the valence vibration of the M–O bond is registered in spinel CoCr_2O_4 , which is the evidence of a stronger bond due to larger overlapping of orbitals $2p\pi - 3d\pi$ of the Cr atom than $2p\sigma - 3p\sigma$ of the Al atom.

The x-ray phase analysis established for $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$ a linear dependence of the parameter a of the elementary cubic cell of the crystalline lattice of spinel on the number of Cr^{3+} atoms replacing Al^{3+} . The parameter a determined based on two lines hkl has the minimum value in spinel CoAl_2O_4 (equal to 8.21 ± 0.01 Å) and the maximum value in CoCr_2O_4 (8.44 ± 0.01 Å). The concentration dependence of the parameter a obeys the Begard rule, which is the evidence of the formation of solid solutions $\text{CoAl}_{2-x}\text{Cr}_x\text{O}_4$.

Taking into account the data of x-ray phase, IR spectroscopy, and differential thermal analysis, as well as the chemical analysis data, the scheme of the spinel formation from hydroxycarbonates can be represented as follows:



In heat treatment of $\text{NH}_4\text{CoM}_2(\text{OH})_5(\text{CO}_3)_2$ the spinel structure is formed only due to the removal of NH_4^+ , CO_3^{2-} , and OH^- , whereas in the synthesis of spinel from oxides or hydroxides, the formation of spinel takes place as a result of reciprocal diffusion of cations on the surface of oxides, which involves high energy consumption and requires increased temperatures [8].

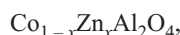
TABLE 2

Sample	Empirical formula of spinel	Temperature, °C	Color (visually)	Color characteristics				
				X	Y	Z	wavelength, nm	color purity, %
1a	CoCrAlO_4	1000–1100	Emerald-green	11.93	14.15	26.17	484	23
1b	CoCrAlO_4	1100	The same	11.93	14.15	26.17	484	23
1c	CoCrAlO_4	1100	"	11.93	14.15	26.17	484	23
2	$\text{CoCr}_{1.5}\text{Al}_{0.5}\text{O}_4$	1000–1100	"	11.93	14.15	26.17	484	23
3	CoCr_2O_4	1000–1100	"	11.93	14.15	26.17	484	23
4	CoAl_2O_4	950–1000	Blue – light-blue	11.70	12.22	29.40	478	20
5	$\text{CoAl}_2\text{O}_4 \cdot 0.5\text{Al}_2\text{O}_3$	950–1000	The same	11.70	12.22	29.40	478	20
6	$\text{CoCr}_{0.5}\text{Al}_{1.5}\text{O}_4$	1100	Emerald green	12.90	15.00	27.00	483	24
7	$\text{CoAl}_2\text{O}_4 \cdot 25\text{ZnAl}_2\text{O}_4 \cdot 0.5\text{Al}_2\text{O}_3$	950–1000	Blue – light-blue	13.34	12.81	36.75	472	22
8	$\text{Co}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$	950–1000	Bright sky-blue	22.00	24.00	66.80	479	33
9	$\text{Co}_{0.09}\text{Mg}_{0.91}\text{Al}_2\text{O}_4$	950–1000	Blue – light-blue	30.48	33.50	53.44	484	15
10	$\text{Co}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4$	950–1000	Blue – light-blue	11.70	12.78	29.90	478	22
11	$\text{Co}_{0.33}\text{Mg}_{0.67}\text{Al}_2\text{O}_4$	950–1000	Bright sky-blue	22.50	24.80	66.40	480	33
Sample	–	1300–1380	The same	22.50	24.80	66.80	480	33

It is established that the color of spinel pigments after firing depends on the concentration of the initial solutions, the temperature and pH of precipitation, and the heat treatment temperature (Table 2). The color tone, color purity, and brightness of spinel samples depend on the content of Mg^{2+} and Zn^{2+} replacing Co^{2+} in the tetrahedral positions, as well as on the ratio of Cr^{3+} and Al^{3+} in the octahedral positions. The spinel samples of the following compositions synthesized from ammonia hydroxycarbonates are bright and pure in color:



where $0.67 \leq x \leq 0.80$, $0 \leq y \leq 2$;



where $0.20 \leq x \leq 0.25$.

The color characteristics of the samples of the composition $\text{Co}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ – $\text{Co}_{0.5}\text{Mg}_{0.5}\text{Al}_2\text{O}_4$ are identical to the reference standard (No. 256 – sky-blue fire-resistant pigment in the Catalog of Inorganic Color Pigments), although the mass content of cobalt oxide (10 – 16%), which is the most expensive component, in the samples is 2 – 3 times lower than in the reference standard. The formation of the spinel structure occurs under the heat treatment temperature of 950 – 1000°C for 1.5 – 2 h.

The samples of spinels containing 0.3 – 2.0 moles of Cr^{3+} have an emerald-green color, and the heat treatment temperature for obtaining a saturated color is 1100 – 1150°C.

Based on the research performed and the tests carried out at the Khrompik JSC (Pervouralsk, current name “Russkii Khrom – 1915”) a waste-free technology has been developed for producing cobalt pigments with a closed water-circulation system. The process consists of the following stages: precipitation of ammonia hydroxycarbonates at temperatures

of 60 – 70°C, filtration and washing of the precipitates, drying of the precipitate at a temperature of 105 – 120°C, soft milling using rolls, and thermal treatment at 950 – 1000°C for 0.5 – 1 h with the production of the finished pigment. The waste gases in the production of cobalt pigments are ammonia and carbon dioxide, which are formed in the dissolution of ammonia hydroxycarbonate, precipitation of ammonia hydroxycarbonate, and thermal treatment. Therefore, the technology implies the recuperation of waste gases CO_2 and NH_3 and the production of ammonium hydroxycarbonate, as well as the utilization of ammonium sulfate and making a commodity product, namely, gypsum. The technological scheme provides for a closed water-circulation system.

REFERENCES

1. V. A. Rakhmanov, “Change of color of pigments of the $\text{CoO} - \text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$ system,” *Steklo Keram.*, No. 11, 22 – 25 (1991).
2. T. Horiuchi, T. Sugiyama, and H. Takashima, “Synthesis of $\text{NH}_4(\text{Al}, \text{Cr})\text{CO}_3(\text{OH})_2$ and the formation process of $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ solid solution by thermal decomposition of that compound,” *J. Ceram. Soc. Jap.*, **96**(8), 881 – 884 (1988).
3. Yu. Yu. Lur’e, *Analytical Chemistry of Industrial Sewage Water* [in Russian], Nauka, Moscow (1984).
4. L. F. Koroleva, *Theory and Practice of Gas Analysis* [in Russian], Ekaterinburg (2002).
5. E. N. Yustova, *Tables of Main Colorimetric Values* [in Russian], Moscow (1967).
6. L. F. Chekhomova and I. I. Kalinichenko, “Synthesis of spinels $\text{CoAl}_2\text{O}_4 - \text{CoCr}_2\text{O}_4$ from ammonia hydroxycarbonates,” *Izv. Vuzov, Ser. Khimiya Khim. Tekhnol.*, **42**(3), 115 – 119 (1999).
7. L. Spiccia, W. Marty, and R. Giovanoli, “Morphological and thermal investigations of the “active” dimer hydroxide of chromium (III),” *Helv. Chim. Acta*, **70**(7), 1737 – 1744 (1987).
8. N. P. Tomilov and E. T. Devyatkina, “Synthesis of MgAl_2O_4 from coprecipitated hydroxides,” *Izv. Ross. Akad. Nauk, Ser. Neorg. Mater.*, **26**(12), 2556 – 2561 (1990).